

Extractants selection for hyphenated electrothermal atomic absorption method

Research Article

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Abstract: The theoretical approach for extractants selection during hyphenated atomic absorption determination of highly volatile metals (Pb, Cd), hydride- (Sb, Bi) and carbide-forming (Cr) metals using thermodynamic modelling was proposed. The calculated parameter – maximum pyrolysis temperature – can be used for selection of the extractants and chemical modifiers. Using this approach the antimony extract with Brilliant green was modified for which the 1.8-fold sensitivity and 2.6-fold repeatability decreasing while extract sampling in graphite furnace was observed. A chemical modifier – mixture of hydrazine nitrate with the palladium(II) complex with Xylenol orange – was theoretically selected and experimentally tested, which allowed to enhance the maximum pyrolysis temperature on 200°C, to eliminate extract matrix influence. Using this modifier two-fold increasing in sensitivity and 3-fold decreasing in relative standard deviation was achieved while extraction atomic absorption determination.

Keywords: Hyphenated Extraction Atomic Absorption Method • Thermodynamic Modeling
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1. Introduction

Hyphenated electrothermal extraction atomic absorption spectroscopy (extraction-ETAAS) method provides metals determination in the complex multicomponent samples at a level of 10^{-6} – $10^{-10}\%$ with an accuracy of up to 3-25% [1-7]. Unfortunately, direct organic extracts sampling into the graphite furnace involves unavoidable difficulties, thus minimizing the benefit of concentrating effect. The difficulties are often due to (i) significant nonselective absorption of the extractant and removal of high-boiling solvents from the furnace, (ii) losses of some extractable volatile compounds, (iii) wetting and soaking of the graphite pores by the extract, with a consequent distortion of the signal wave shape, a decrease in its intensity and diminution of the determination accuracy [8-12].

The analyte compounds atomization mechanism may differ greatly in aqueous solutions and organic extracts

during ETAAS determination. The wrong extraction system may eliminate the concentrating effect. The theoretical approach for optimal extractants selection based on thermodynamic modelling of high temperature processes in a furnace was developed.

Until now, this selection has been carried out on an empirical basis, usually by complete extraction of analytes. Furthermore, there are no parameters for prediction of efficiency of extracts and their compatibility with the graphite furnace.

The search of predictive parameter can be calculated on the base of thermodynamic modelling results, for preliminary extraction systems selection providing the same sensitivity and repeatability for aqueous solutions and organic extracts, was the goal of this paper. The chemical composition prediction of extracts optimum chemical modifiers in a hyphenated extraction-ETAAS method was also the goal of this research.

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Table 1. Extraction systems for hyphenated ETAAS method.

Extracting agent, solvent	Abbreviation	Extractable element	Extraction conditions	Ref.
Sodium pyrrolidine dithiocarbamate, butyl acetate	SPDC, BuAc	Pb(II), Cd(II), Sb(III), Bi(III)	pH 3 (citrate buffer); equilibration time – 2 min; aqueous/organic phase ratio 10:1	[13]
Tri-<i>n</i>-octyl ammonium chloride, methyl isobutyl ketone	TOACI, MIBK	Cd(II), Bi(III), Sb(III)	2 M HCl; equilibration time – 5 min; aqueous/organic phase ratio 10:1	[14]
Brilliant green, toluene	BG, toluene	Sb(V)	8 M HCl, Sb(V) was reduced by Sn(II) and then oxidized by NaNO ₂ ; equilibration time – 1 min, aqueous/organic phase ratio 50:1	[15]
Diphenylcarbazide, ethanol	DPC, EtOH	Cr(VI)	0.1 M H ₂ SO ₄ ; complex-formation time – 10 min; salting-out agent (NH ₄) ₂ SO ₄ ; aqueous/organic phase ratio 2:1	[16]

2. Experimental procedure

2.1. Reagents and standard solutions

Model analytes were highly volatile metals (Pb, Cd), hydride- (Sb, Bi) and carbide-forming (Cr) metals.

Extraction systems were selected for complete extraction of the elements tested which are different in their extraction mechanisms (chelates and ion associates) and thermal characteristics of the extractants (Table 1).

Standard solutions of lead(II), cadmium(II), bismuth(III), antimony(III) and chromium(VI) were prepared from the certified reference solutions of metal ions at Physico-Chemical Institute of National Academy of Science (Odessa, Ukraine). Standard solution of antimony(V) was prepared in accordance with [17]: 0.1000 g of antimony was dissolved in the hot mixture of concentrated nitric (0.3 mL) and hydrochloric (1 mL) acids. After removal of nitrogen oxides the resulting solution was diluted to the volume (100 mL) with hydrochloric acid (6 mol L⁻¹) to give an antimony(V) content of 1.000 ± 0.005 mg in 1 mL.

The reagents used were reagent grade sodium pyrrolidine dithiocarbamate (Fluka AG, Buchs SG, Switzerland), diphenylcarbazide, tri-*n*-octyl amine (Fluka AG, Buchs SG, Switzerland) and pure grade Brilliant green. The extraction of the ion associates and chelates was performed with the reagent grade organic solvents. All accessory reagents were reagent grade or higher.

2.2. Apparatus

ETAAS measurements were carried out using atomic absorption spectrophotometer Saturn 3 (deuterium background corrector), Solaar M (Zeeman and deuterium background correctors) with the recording of the integrated signal intensity. The light-sources were hollow-cathode lamps LT-2 (Pb, Cd, Bi, Cr) and

electrodeless discharge lamp VSB-2 (Sb). Absorbance of the elements was monitored at the resonance wavelengths 283.5 nm (Pb) 228.8 nm (Cd), 217.6 nm (Sb), 306.7 nm (Bi) and 357.9 nm (Cr).

The experiments were carried out with the use of pyrocoated electrographite (VEB Elektrokohle Lichtenberg, Germany), graphite tubes (Severodonetsk, Ukraine), and pyrocoated and non-coated graphite platforms (Severodonetsk, Ukraine). The solutions tested were sampled with manual sampler P200 on a platform or a pyrocoated graphite furnace wall. Sampling accuracy was ±0.2%.

2.3. Procedures

The extraction of Pb(II), Cd(II), Sb(III) and Bi(III) pyrrolidine dithiocarbamate complexes, ion associates of Cd(II), Bi(III), Sb(III) acidocomplexes with TOACI, Sb(V) with Brilliant green, and Cr(VI) complexes with diphenyl carbazide by two-phase aqueous ethanol was carried out in the presence of the salting-out agent, (NH₄)₂SO₄, as specified in Table 1. The extracts were filtered through a dry filter into a ground-glass weighing cup and immediately analyzed by ETAAS method. The extracts were sampled on a platform or a graphite furnace wall. The atomizer was then heated in three stages: (i) drying at 105-130°C, (ii) pyrolysis at 250-1700°C, and (iii) atomization at 2000-2300°C. At the atomization stage the feed of argon in the inner space of the graphite furnace was turned off.

Thermodynamic modelling (TDM) of the high-temperature processes were carried out as described elsewhere [18,19] using Astra-4 software.

Sensitivity of ETAAS determination was estimated by its characteristic mass m_0 , determined by the integral value of absorbance [20]. Repeatability of element absorbance (A) measurements in the extracts were characterized by relative standard deviation (RSD).

Table 2. Characteristic masses and relative standard deviation (RSD) in volatilization of aqueous solution and organic extracts from the furnace wall (I) and platform (II).

Extract	m^*_0 , pg		RSD, % (n = 5; P = 0.95)					
	aqueous solution		extract		aqueous solution		extract	
	I	II	I	II	I	II	I	II
Cd(PDC)₂-BuAc			18	0.47			28	9.9
(TOAH)₂CdCl₄-MIBK	0.45	0.43	17	0.57	9.9	9.1	30	9.4
Pb(PDC)₂- BuAc	8.0	8.1	34	10	9.5	7.8	25	8.9
Sb(PDC)₃- BuAc			54	15			33	13
(TOAH)₃SbCl₅-MIBK	14	13	52	14	8.6	7.8	34	14
BGSbCl₅-toluene			–	24			–	20
Bi(PDC)₃- BuAc			525	25			–	16
TOAHBiCl₄-MIBK	–	21	–	26	–	8.8	–	11
CrDPC-H₂O-EtOH	2.4**	57***	5.6**	62***	7.9**	14***	7.2**	26***

Measuring conditions: highest-grade inert gas argon; D₂-corrector; pyrocoated graphite tubes and platforms; integrated signal recording; "gas-stop" mode of operation.

* theoretical m^*_0 for Cd, Pb, Sb, Bi, and Cr are 0.46, 10, 13, 19, and 1.62 pg, respectively (B.V. L'vov [20]);

** pyrocoated electrographite furnace;

*** platform (with no coating).

3. Results and discussions

3.1. Metrological characteristics of Pb(II), Cd(II), Sb(III,V), Bi(III) and Cr(VI) ETAAS determination in organic extracts

The organic extracts examination in the graphite atomizers is accompanied by some problems which can considerably affect determination of sensitivity [8,9,11,12]. Hence, analytical signal measurement repeatability and sensitivity of Pb, Cd, Sb, Bi, and Cr ETAAS determination in the organic extracts were also studied.

Table 2 contains the data on changes in sensitivity and reproducibility for aqueous solutions and the corresponding extracts evaporated from the graphite furnace wall and platform.

Examination of the extracts characteristic masses revealed that the best sensitivity, approaching the theoretical value and that for aqueous solutions, is common for the extracts of the high-volatility elements (Pb and Cd) only under their volatilization from the platform under "stabilized temperature platform furnace" concept conditions [21]. Close agreement was also observed for repeatability of Cd and Pb measurements for aqueous solutions and organic extracts.

The sensitivity of bismuth determination in the extract closely resembles that in aqueous solution for samples volatilization from the platform. It should be noted that for hydride-forming elements (Bi and Sb) the

measurement precision was found to deteriorate: RSD for the extracts were 1.5-2.6 times higher than those for aqueous solutions even for volatilization from the platform. This is understood to be due to the inverse atomization mechanism of the elements [22].

The values of m^*_0 for Sb(III,V) extracts were dependent on the nature of the extractant: 1.8 fold decrease in sensitivity was detected only for the extract of Sb(V) chloride acidocomplex with BG as compared to the aqueous solutions.

In chromium extraction by aqueous ethanol two-phases system the surface conditions of the atomizer (with or without pyrocoating and quality of the coating) are responsible for sensitivity and repeatability of chromium ETAAS determination in the extract.

3.2. The prediction of pre-atomization compounds chemical composition in extraction-ETAAS analysis of organic extracts

Thermodynamic modelling (TDM) of high-temperature processes on the atomizer surface makes it possible to estimate qualitative and relative quantitative composition of the condensed and gas phase in the analytical zone. The essence of TDM consists of determination of equilibrium composition of complex multicomponent heterogeneous systems by entropy maximization or minimization of Gibbs energy of the thermodynamic system.

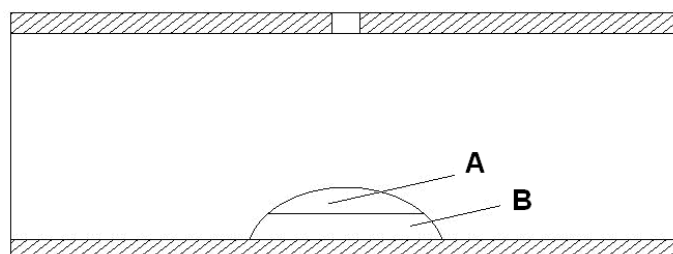


Figure 1. Schematic of sample thick layer the in graphite furnace: contacting (top) zone (A) and non-contacting (bottom) zone (B) with the atomizer surface.

For thermodynamic system which is realized in the graphite furnace during pyrolysis stage the Langmuir conception of thin boundary layer with a short equilibration time can be used in modelling thermodynamic systems under study. The boundary layer can be divided into two zones (thermodynamic subsystems) – contacting (top – A) and non-contacting (bottom – B) with the surface of the atomizer (Fig. 1).

This approach simulates the presence of sufficiently thick sample layer (matrix, chemical modifier, analyte) on the graphite tube surface. The calculations of thermodynamic subsystem equilibrium composition were then performed in accordance with the sequence of condensed sample thermal transformations. The thermodynamic subsystem initial composition was set according to [18,19]. The atomization stage TDM is based on the assumption of high-rate equilibration setting under impulse introduction of a certain amount of substance in the atomizer high-temperature zone.

Experiments on TDM were carried out with the extracts (chelates and ion associates) and aqueous solutions of the elements tested (antimony(III) sulfate, antimony(V) hydroxychloride, potassium dichromate, and lead(II), cadmium(II) and bismuth(III) nitrates). The organic solvent was assumed to be completely removed from the system at the onset of pyrolysis stage. Modeling experiments on possible pyrolysis reactions in the BGSbCl₆ extract were additionally carried out with the model system at an intentionally increased (1.5-fold) mole fraction of hydrogen. According to recommendations given in [18,19] for the bottom zone, the surface of the atomizer was contacted with a specific amount of carbon, which was in excess of ten-fold over than the sample matrix. Calculation of multi-component high-temperature equilibrium was performed at a pressure of 10⁵ Pa within the temperature range of 100-1900°C. Table 3 shows the results of modeling experiments in terms of the analyte predominant compounds in the condensed and gas phase of the conventional zone at a maximum pyrolysis temperature (T_p^{\max}). Mole fractions of the analyte predominant compounds were no less than 0.001 that in the analyte

with the maximum mole fraction. Table 3 also contains information about the experimental ratios of metals ETAAS determination sensitivities of the extract to those in the aqueous solution expressed as the ratio of the corresponding characteristic masses, ($m_0^{\text{ex}} / m_0^{\text{w}}$).

In addition, Table 3 gives the experimental maximum pyrolysis temperature in antimony, bismuth, cadmium and chromium ETAAS determination in aqueous solutions and organic extracts.

An agreement between the calculated and experimental temperatures (T_p^{\max}) for organic extracts volatilization was considered as a validity criterion for the model system. Data on TDM of the aqueous solutions were used for ascertaining the thermodynamic subsystem (zone) responsible for the tested element free atoms formation or their volatile molecular species. Thus, calculated and experimental T_p^{\max} for cadmium nitrate in the bottom zone is not much different from each other (400 and 350°C, respectively) and, hence, the modelling results for the bottom zone were used in consideration of the Cd(PDC)₂ and (TOAH)₂CdCl₄ extracts. For hydride-forming bismuth the top zone is information-bearing area of the vaporizing sample, which is in contact with the inert gas. In the case of Bi(NO₃)₃ the calculated and experimental T_p^{\max} (900 and 1100°C, respectively) in the top zone does not differ markedly and the same is true both for Bi(PDTC)₃ (800 and 830°C) and TOAHBiCl₄ (900 and 940°C). This makes it possible to use T_p^{\max} in prediction of efficiency of the combined use of the extraction system with ETAAS for highly volatile (Pb, Cd) and hydride-forming (Sb, Bi) elements.

It should be noted that in the case of carbide-forming chromium in K₂Cr₂O₇ solution the calculated and experimental T_p^{\max} (1300°C) were found to be the same (1300°C) for the top zone, whereas those for the bottom zone differ from one another. In addition, the calculated T_p^{\max} (1600°C) for chromium(VI) extract is in a rather poor agreement with experimental value (1300°).

With sulfur-containing chelates the experimental T_p^{\max} for lead and cadmium extracts are somewhat higher than those of their aqueous solutions. Thus

Table 3. Thermochemical processes thermodynamic modeling, and experimental values of relative sensitivity and maximum pyrolysis temperature.

Extraction system	Zone	Calculated T_p^{\max} , °C	Experimental T_p^{\max} , °C	Predominant analyte compounds at T_p^{\max}		$\frac{m_0^{\text{ex}}}{m_0^{\text{w}}}$
				condensed phase	gas phase	
Pb(NO₃)₂	A	700	640	PbO	Pb ₂ O ₂ , PbO	–
	B	600		Pb	Pb	
Pb(PDTC)₂	A	800	850	PbO	Pb ₂ O ₂ , PbO, PbO ₂	1.2
	B	800		PbS	PbS, PbS ₂	
Cd(NO₃)₂	A	700	350	CdO	Cd	–
	B	400		Cd	Cd	
Cd(PDTC)₂	A	900	850	CdO	Cd, CdO ₂ H ₂	1.1
	B	900		CdS	Cd	
(TOAH)₂CdCl₄	A	400	630	CdCl ₂	CdCl ₂	1.3
	B	600		CdCl ₂	Cd, CdCl ₂	
Bi(NO₃)₃	A	900	1100	Bi ₂ O ₃	Bi ₄ O ₆ , BiO, Bi	–
	B	1400		Bi ₂ O ₃	Bi ₄ O ₆ , BiO, Bi	
Bi(PDTC)₃	A	800	830	Bi ₂ O ₃	Bi ₄ O ₆ , BiO, Bi	1.2
	B	400		Bi ₂ S ₃ , Bi	BiS, Bi ₂ , Bi	
TOAHBiCl₄	A	900	940	Bi ₂ O ₃	BiCl ₃ , BiCl, Bi ₄ O ₆	1.2
	B	600		Bi	BiCl, Bi ₂ , Bi	
H[Sb(SO₄)₂]	A	800	900	Sb ₂ O ₄	Sb ₄ O ₆	–
	B	900		Sb	Sb ₄ , Sb ₂ , SbS	
Sb(PDTC)₃	A	800	870	Sb ₂ O ₄	Sb ₄ O ₆	0.98
	B	600		Sb	Sb ₄ , Sb ₂ , SbS	
(TOAH)₃SbCl₆	A	900	930	Sb ₂ O ₄	Sb ₄ O ₆	1.1
	B	700		Sb	SbCl ₃ , SbCl ₄ , Sb ₄	
H[Sb(OH)Cl₅]	A	600	850	Sb, Sb ₂ O ₃	SbCl ₃ , Sb ₄ O ₆ , SbCl	–
	B	700		Sb	SbCl ₃ , SbCl	
BGSbCl₆	A	200	650	Sb, Sb ₂ O ₃	SbCl ₃	1.8
	B	200		Sb	SbCl ₃	
BGSbCl₆ + H*	A	700	–	Sb ₂ O ₅	SbCl ₃	–
	B	800		Sb	SbCl ₃ , SbCl	
K₂Cr₂O₇	A	1300	1300	Cr ₂ O ₃	CrO ₃	–
	B	1600		Cr ₃ C ₂	Cr	
CrDPC, H₂SO₄	A	1600	1300	CrS, Cr ₃ C ₂	Cr, CrS, CrS ₂	2.3
	B	1600		CrS, Cr ₃ C ₂	Cr, CrS, CrS ₂	

m_0^{ex} and m_0^{w} is the characteristic mass of the element for evaporation of the extract and aqueous solution, respectively;

* model system.

T_p^{\max} for lead pyrrolidine dithiocarbamate complex and lead aqueous solution were found to be 850°C and 640°C, respectively. This is probably due to the pyrolytic formation of additional carbon substrate on the platform, resulting in a change of the heat transfer conditions. This is in close agreement with those available from the literature [23], where an increase in T_p^{\max} was

also observed in atomization of sulfur-containing chelates (Cd(II), Cu(II), Fe(III), Mn(II), Ni(II), and Pb(II) hexamethylene dithiocarbamates). For the extracts of hydride-forming elements these parameters are similar in value.

Thermodynamic modelling makes it possible to predict chemical composition of pre-atomization metal

compounds in the condensed phase at the end of extracts pyrolysis and expected metal compounds responsible for the analyte losses during the extracts ETAAS analysis. It is clear that the composition of tested elements pre-atomization compounds can be varied in comparison with aqueous solutions. In the extracts with sulfur-containing reagent, SPDC, both sulfides and oxides can be formed in the condensed phase. According to modeling, antimony(III) and bismuth(III) pyrrolidine dithiocarbamates pyrolysis can result in the formation of oxides (Sb_2O_3 and Bi_2O_3). As for chromium, the proportion of thermostable chromium carbide which is formed both in the bottom and top zone can be increased. Moreover, an addition of sulfuric acid in the extract gives rise to the formation of chromium sulfides, CrS and CrS_2 , in the condensed phase.

In the case of hydride-forming antimony and bismuth in the extracts of TOAHBiCl_4 and $(\text{TOAH})_3\text{SbCl}_6$ the composition of the pre-atomization compounds remains near unchanged in comparison with the aqueous solutions. According to modeling data, however, bismuth monochloride can be formed in the gas phase at elevated temperatures above 900°C .

The modelling results suggest that the presence of chloride ions in the organic extracts of ion associates of TOAHBiCl_4 and $(\text{TOAH})_3\text{SbCl}_6$ must give rise to no loss in analyte at the early stages of analysis. Experimental data support this conclusion: antimony and bismuth sensitivity in the extracts remained near the same as compared with aqueous solutions (characteristic mass ratio is approximately unity).

With $(\text{TOAH})_2\text{CdCl}_4$ extract, the composition of pre-atomization compound changes compared to aqueous solution of Cd(II) . In the condensed phase the pyrolysis of the extract results in the formation of CdCl_2 which passes into gas phase at a higher temperature than in the case of aqueous solution - 600 and 400°C , respectively. Cadmium enters into the gas phase in the form of cadmium chloride and elemental cadmium. Since the cadmium chloride proportion is high, the sensitivity of the cadmium determination in the extract decreases slightly.

A different behavior is observed for the ion associate of Sb(V) chloride complex with the BG cation. In pyrolysis of the BGSbCl_6 extract, the composition of the condensed and gas phases is changed. Thus, the modeling shows that only Sb_2O_3 is formed in the condensed phase during pyrolysis of Sb(V) aqueous solution, whereas pyrolysis of BGSbCl_6 extract results in the formation of elemental Sb and Sb_2O_3 . Changes in the gas phase are more essential: antimony vaporizes in the form of Sb_4O_6 from the aqueous solution, whereas vaporization of the

extract results in the formation of SbCl_3 even in pyrolysis early stages at 200°C . Calculated maximum pyrolysis temperature for the extract is considerably lower. This is experimentally supported by the fact that determination of sensitivity of antimony in this system is decreased by a factor of 1.9 (Table 3).

The difference in the behavior of two chlorine-containing extracts, $(\text{TOAH})_3\text{SbCl}_6$ and BGSbCl_6 , is due to mole fraction of hydrogen in the extractable substance. Evidence for this is the model system « $\text{BGSbCl}_6 + \text{H}$ », in which an initial mole fraction of hydrogen was increased 1.5-fold. Table 3 shows that the calculated T_p^{\max} for this system is higher (700°C). A higher T_p^{\max} (650°C) for BGSbCl_6 extract in comparison with the calculated value (200°C) is explained by higher mole fraction of hydrogen due to the presence of the latter in the argon.

To summarize, at the initial stage of selection the calculated parameter T_p^{\max} for high-volatility and hydride-forming compounds makes it possible to evaluate the efficiency of the combination of extractant and electrothermal atomizer. However, this is not true for carbide-forming chromium. Modeling experiments permit also task-oriented selection of the reagent for chemical modification of the extracts and prediction of its efficiency.

3.3. Chemical modification of organic extracts

The basic reason for chemical modification of hydride-forming elements extracts is the necessity for prevention of their losses by the use of analyte thermostabilization. In addition, the modifiers make it possible to regulate removal of matrix components in order to eliminate their depressing effects.

In antimony determination the modification of the extraction system Sb(V) with the BG cation in toluene and based on the TDM data the compounds with high hydrogen mole fraction were selected as chemical modifiers (CM). Increased hydrogen mole fraction relative to that of antimony (model system « $\text{BGSbCl}_6 + \text{H}$ », Table 3) results in an increase in the calculated maximum allowed temperature of pyrolysis, T_p^{\max} . This, in turn, implies that the amount of volatile antimony compounds (namely, antimony halides) in the gas phase of the analytical zone is decreased.

Saturated hydrocarbon, dodecane, was selected as a CM. For convenience of modifier introduction it is desirable to use a liquid compound. Dodecane ($\text{C}_{12}\text{H}_{26}$, $\omega(\text{H})$ 15,3%, bp 216°C [24]) meets the requirements. A mixture of hydrazine nitrate with the palladium(II) complex with Xylenol orange (PdXO) was also studied. The latter has been used for atomization processes modification in Mo, Mn, Cr, Ni, Pb, and Cd ETAAS determinations in different objects [25]. Hydrazine

Table 4. Efficiency of Sb(V) hyphenated ETAAS determination (solution of BG in toluene).

Chemical modifier	$\Delta T_p^{\max}, ^\circ\text{C}$	$(A-A_{\text{blank}})/A_0$		RSD ^o /RSD	
		integral recording	amplitude recording	integral recording	amplitude recording
$\text{C}_{12}\text{H}_{26}$	0	1.1	1.4	1.1	1.5
$\text{N}_2\text{H}_5\text{NO}_3 + \text{PdKO}$	200	1.1	1.9	1.5	3.1

pyrolysis can increase the hydrogen gas content in the analytical zone as well as reduce palladium in the complex.

Taking into account the fact that the main loss of antimony chloride was observed later during the drying step, CM was first sampled on the platform and then the extract was sampled. Data on efficiency of the selected chemical modifiers in antimony extraction atomic absorption determination is presented in Table 4.

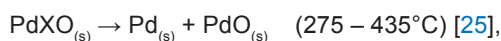
Modifiers tested efficiency was evaluated by antimony analytical signal increase in the modifier presence $(A-A_{\text{blank}})/A_0$, where A and A_0 is the antimony absorbance in the extract with and without CM, respectively; A_{blank} is the absorbance of the blank run.

In addition, an increase in extract maximum pyrolysis temperature ΔT_p^{\max} as compared to the extract without CM, and an improvement in analytical signal measurement repeatability in terms of the relative standard deviation ratio with and without modifier, RSD^o/RSD, were also considered. The parameters were calculated from analytical signals integral or amplitude recordings.

The sensitivity and repeatability of antimony hyphenated ETAAS determination in terms of integral signal recordings are relatively unaffected by dodecane. Under these conditions there is no increase in sensitivity when the mixed modifier $\text{N}_2\text{H}_5\text{NO}_3 + \text{PdXO}$ is added. In this case the chemical modifiers added cause an improvement in the form of the peak, resulting in 1.4- and 1.9-fold increase of sensibility in determinations on the basis of amplitude recording of the peak for dodecane and the mixture of $\text{N}_2\text{H}_5\text{NO}_3$ with PdXO, respectively. An improvement in the form of the peak gives rise to an increase in measurements repeatability by a factor of 1.5 and 3.1 for dodecane and the mixed modifier, respectively.

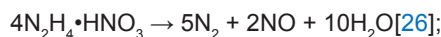
Action of antimony extract mixed modifier ($\text{N}_2\text{H}_5\text{NO}_3 + \text{PdXO}$) appears to be due to a number of processes:

– PdXO complex pyrolysis and reduced palladium formation with or without participation of hydrazine:

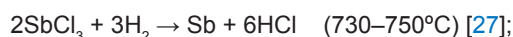


the indexes (s) mean solid state

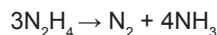
– hydrazine nitrate decomposition on heating above 200°C:



– possible reduction of Sb(V) to Sb(III) by hydrazine [26] followed by reduction of Sb(III), for example, by the reaction:



– hydrazine reduction in the presence of the catalysts – platinum-group metals [26]:



These processes give rise to an increase in the reducing properties of analytical zone and facilitate the chlorides stripping in the form of volatile HCl. Based on amplitude recording data, chloride removal results in near two-fold increase in sensitivity of antimony determination in the extract and 3-fold decrease in RSD. The observed effects are less pronounced in “stabilized temperature platform furnace” conditions. However, the mixed modifier favors the repeatability improvement even under these conditions. Such mixed modifier is more efficient than dodecane. Moreover, in the case of mixed CM from hydrazine and PdXO an additional antimony thermal stabilization due to modifying effect of palladium was observed. Addition of CM into the system containing the BGSbCl₆ extract gives rise to an improvement in the form of the analytical signal: the peaks become narrow and take a regular shape.

4. Conclusions

Maximum pyrolysis temperature, T_p^{\max} , calculated from data on thermodynamic modeling, can be used for selection of the extractants and chemical modifiers in hyphenated ETAAS method for the extracts of Cd(II),

Pb(II), Bi(III), and Sb(III) pyrrolidine dithiocarbamates, ion associates of Cd(II), Sb(III,V), and Bi(III) acidocomplexes with tri-*n*-octyl ammonium chloride or Brilliant Green. The mixture of hydrazine nitrate (0.001 mol L⁻¹) and Pd(II) complex with Xylenol orange (0.001 mol L⁻¹) can be served as an efficient

chemical modifier, capable of enhancing sensitivity and repeatability of Sb determination in the extract of ionic associate of chloride acidocomplex with Brilliant Green. The modifier causes 2-fold sensitivity increase and 3-fold repeatability improvement of Sb determinations in comparison with non-modified extracts.

References

- [1] Zh. Fan, W. Zhou, *Spectrochim. Acta Part B* 61, 870 (2006)
- [2] I. De La Calle, F. Pena-Pereira, N. Cabaleiro, I. Lavilla, C. Bendicho, *Talanta* 84(1), 109 (2011)
- [3] N.N. Meeravali, M.A. Reddy, S.J. Kumar, *Anal. Sci.* 23(3), 351 (2007)
- [4] M.S. Tehrani, P.A. Azar, S.W. Husain, F. Shafaei, *Asian J. Chem.* 22, 6302 (2010)
- [5] A.N. Anthemidis, G.A. Zachariadis, J.A. Stratis, *J. Anal. At. Spectrom.* 18, 1400 (2003)
- [6] A.N. Gorbachevskii, N.F. Kushchevskaya, V.A. Doroshchuk, *J. Water Chem. Technol.* 31, 244 (2009)
- [7] E.M. Martinis, P. Bertón, J.C. Altamirano, R.G. Wuilloud, U. Hakala, *Talanta* 80, 2034 (2010)
- [8] A.B. Volynsky, B.Ya. Spivacov, Yu.A. Zolotov, *Talanta* 31, 449 (1984)
- [9] J. Komarek, L. Sommer, *Talanta* 29, 159 (1982)
- [10] N.V. Meshchaninova, A.S. Alemasova, *Analytika i kontrol* 10, 3 (2006) (in Russian)
- [11] E. Tserovsky, S. Arpadjan, I. Karadjova, *J. Anal. At. Spectrom.* 8, 85 (1993)
- [12] E. Tserovsky, S. Arpadjan, *J. Anal. At. Spectrom.* 6, 487 (1991)
- [13] ISO 8288:1986 (International Organization for Standardization (ISO), 1986)
- [14] A.S. Alemasova, I.A. Shevchuk, *Khimicheskie reaktivy v atomno-absorbicjonnom analize* (NMK VO, Kiev, 1992) (In Russian)
- [15] GOST 6689.15-92 (Izdatel'stvo standartov, Moscow, 1992) (In Russian)
- [16] Pat. № 3896, MPK 7 G01N33/20. 15.12.2004 (In Ukrainian)
- [17] GOST 4212-76 (Izdatel'stvo standartov, Moscow, 1987) (In Russian)
- [18] A.A. Pupyshev, *J. Anal. Chem.* 55, 706 (2000)
- [19] M.Yu. Burylin, Z.A. Temerdashev, A.A. Pupyshev, A.A. Kaunova, S.A. Obogrelava, *J. Appl. Spectrosc.* 73, 760 (2006)
- [20] B.V. L'vov, V.G. Nikolaev, E.A. Norman, L.K. Polzik, M. Mojica, *Spectrochim. Acta Part B* 41, 1043 (1986)
- [21] W. Slavin, D.C. Manning, G.R. Carnrick, *At. Spectrosc.* 2, 137 (1981)
- [22] A.Kh. Gil'mutdinov, Yu.A. Zaharov, V.P. Ivanov, A.V. Voloshin, *Zh. Anal. Kh.* 49, 157 (1994) (In Russian)
- [23] I. Karadjova, G. Zachariadis, G. Boskou, *J. Anal. At. Spectrom.* 13, 201 (1998)
- [24] M. Ash, I. Ash, *Handbook of Solvents* (Synapse Information Resources, Endicott, NY, 2003)
- [25] N.D. Shchepina, *Izvestiya Vuzov. Kh. Khim. Tehnolog.* 48, 7 (2005) (In Russian)
- [26] L.F. Audrieth, B.A. Ogg, *The chemistry of hydrazine* (Wiley, 1951)
- [27] N.C. Norman, *Chemistry of Arsenic, Antimony and Bismuth* (Thomson Science, London, 1998)